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NANOSTRUCTURED AND NANOCOMPOSITE LIGHT-METAL BASED COMPOUNDS FOR HYDROGEN STORAGE

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HYDROGEN – THE FUEL OF THE FUTURE

With the concerns of the global climate warming it is absolutely indispensable for the mankind to develop new clean energy sources other than fossil fuels.

The consensus of opinion is setting on hydrogen for either supplying fuel cells or internal combustion engines as the way forward. According to many in the scientific community we are now at the verge of a new hydrogen age. Extensive research efforts are lying down the foundation of the next industrial revolution in the application of hydrogen as the fuel of the future.

HYDROGEN STORAGE FOR PROTON MEMBRANE EXCHANGE (*PEM*) FUEL CELLS FOR VEHICULAR (MOBILE) APPLICATIONS

Excerpts from Ritter et al, *Materials Today*, September 2003, pp.18-23

"In recent years, months, weeks, and even days, it has become increasingly clear that hydrogen as an energy carrier is "in " and carbonaceous fuels are "out". The hydrogen economy is coming with the impetus to transform our fossil energy-based society, which inevitably will cease to exist, into a renewable energy-based one.

However, hydrogen storage is proving to be one of the most important issues and potentially biggest roadblock for the implementation of a hydrogen economy. Of the three options that exist for storing hydrogen, in a solid, liquid and gaseous state, the former is becoming accepted as the only method potentially able to meet the gravimetric and volumetric densities of the recently announced FreedomCar goals; and of all known hydrogen storage materials, complex hydrides may be the only hope".

HYDROGEN STORAGE FOR *PEM* FUEL CELL-POWERED VEHICLES

The highest *volumetric* density required

Storage system	Volumetric density ($kgH_2\ m^{-3}$)	Drawbacks
Compressed hydrogen gas under 80 MPa pressure	~40	Safety problems (enormous pressures required)
Liquid hydrogen at cryogenic tank at -252^{0}C (21K):	~71	Large thermal losses (open system!)
Solid metal/intermetallic hydrides	~80-150	None

HIGH VOLUMETRIC HYDROGEN DENSITY FOR VEHICLES

~4 kg of hydrogen → range ~480 km (300 miles)

Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car

Toyota press, 33rd Tokyo Motor Show, 1999; L.Schlapbach and A. Züttel, Nature,414, 353-358 (2001)

HYDROGEN FOR *PEM* FUEL CELLS-
Gravimetric density

The highest *gravimetric* density: light metal-based hydrides

Metal-hydrogen system	Hydride	Theoretical hydrogen capacity (wt%)	Density of hydride (g/cm^3)	Decomposition temperature (^0C)
Li-B-H	$LiBH_4$	18.4	0.67	380
Mg-B-H	$Mg(BH_4)_2$ or MgB_2H_8	15.3	0.99	300-800 (?)
Na-B-H	$NaBH_4$	10.6	1.07	400
Mg-Fe-H	Mg_2FeH_6	5.4	2.72	320
Mg-Mn-H	Mg_3MnH_7	5.2	2.30	280
Mg-Co-H	Mg_2CoH_5	4.5	2.70	350 (?)

HYDROGEN FOR *PEM* FUEL CELLS-
Requirements for metal/intermetallic hydrides

- **World Energy Network (Japan):**

Hydrogen capacity > 3wt%; desorption temp. ~100^{0}C; 5000 cycles life

- **International Energy Agency:**

Hydrogen capacity > 5wt%; desorption temp. < 150^{0}C; 1000 cycles life

- **Department of Energy (USA):**

Hydrogen capacity > 6wt%

HYDROGEN FOR *PEM* FUEL CELLS-
Metal/intermetallic hydrides-Conclusions

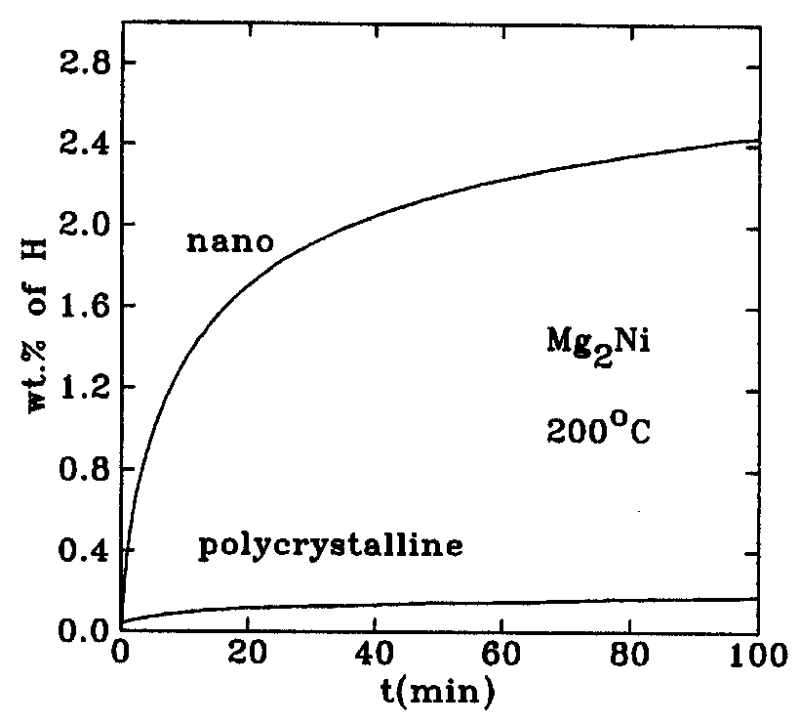
- All light metal-based hydrides have excellent hydrogen storage capacities sometimes exceeding those required by various agencies for vehicular applications
- All of them have a fatal drawback: too high desorption temperature!
- Their desorption kinetics are slow for polycrystalline alloys

HOW CAN WE IMPROVE KINETICS AND DESORPTION TEMPERATURE ?!

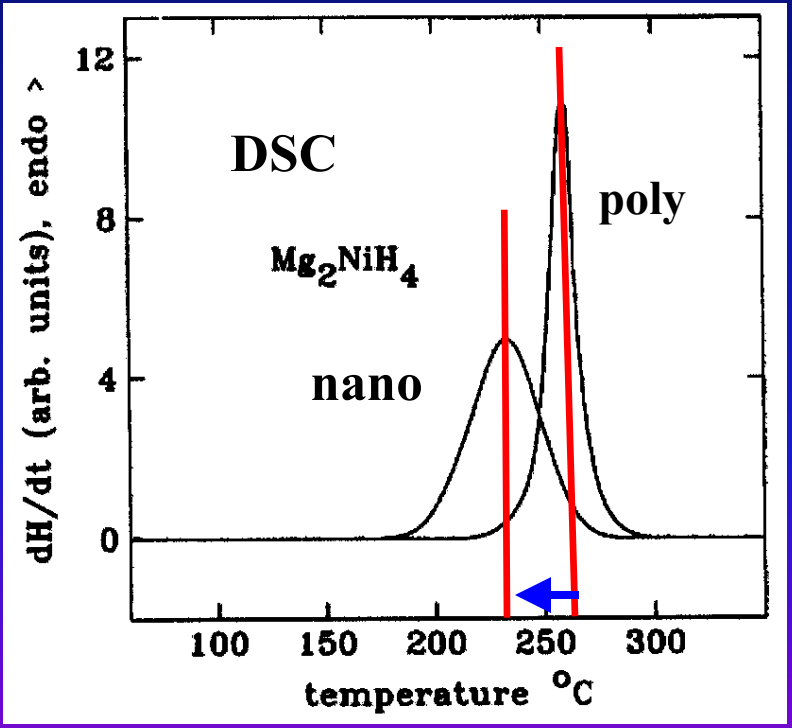
BEHAVIOR OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES

Zaluska et al., Appl. Phys. A 72 (2001) 157-165 (review paper)

Absorption kinetics



Desorption temperature



METHODS OF SYNTHESIS OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES

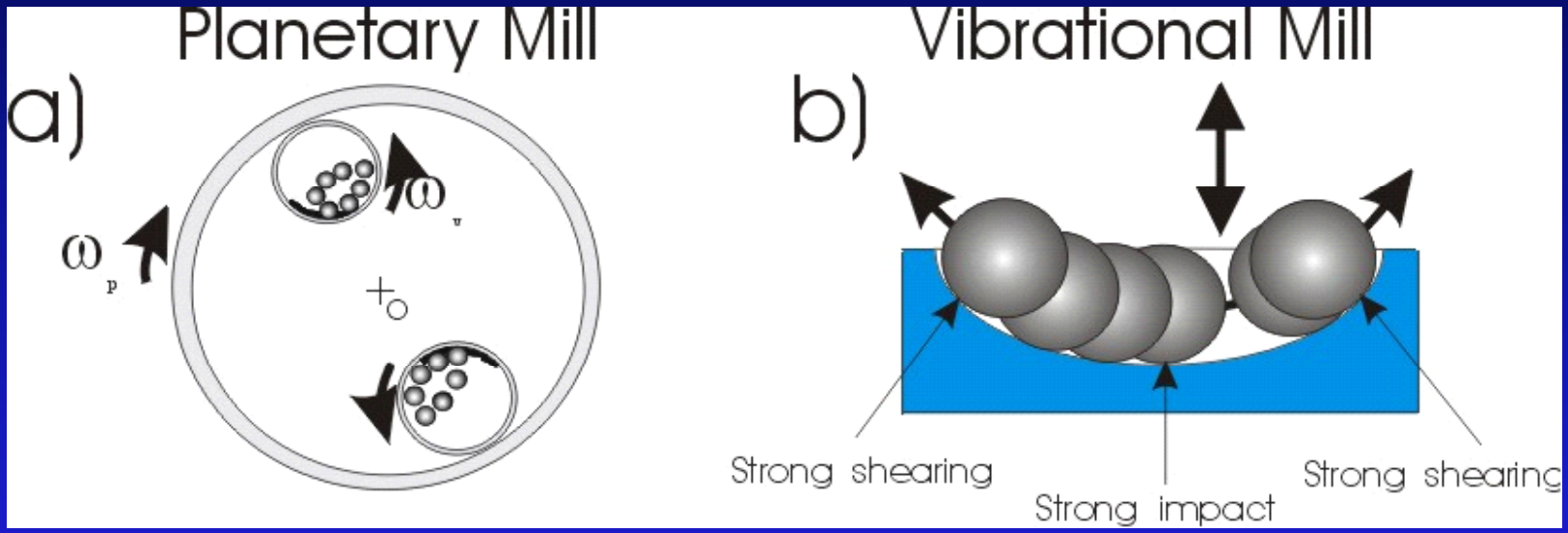
Definition: ***Nanostructured/nanocomposite*** **means that each phase present in the individual powder particle is in the form of** ***grains*** **with** ***nanometer*** **size; one particle is one** ***nano-polycrystal***

1.Two-step: mechanical alloying (MA) of elemental metal powders or milling (MM) of bulk alloys under protective gas (Ar, He) ; subsequent hydrogenation in a separate step under appropriate pressure of H_2

2.One-step: mechanical alloying/milling of elemental metal powders/bulk alloys directly under hydrogen – Reactive Mechanical Alloying/Milling (RMA/RMM) – cost reduction and ease of hydride formation - preferable

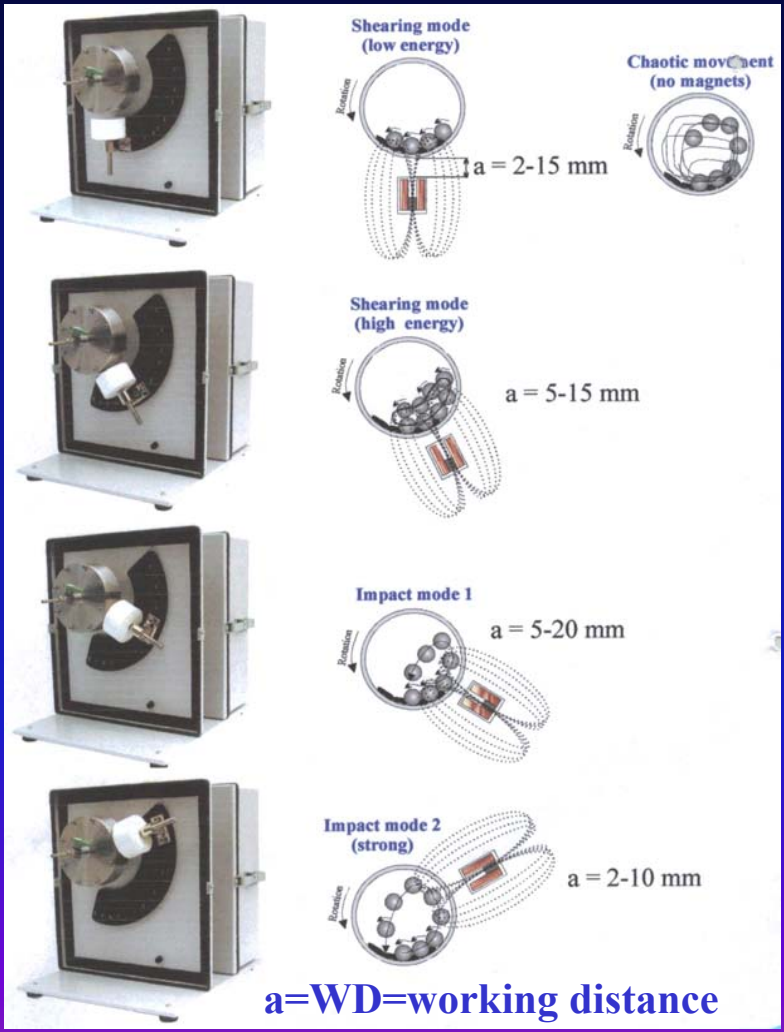
METHODS OF SYNTHESIS OF NANOSTRUCTURED/NANOCOMPOSITE HYDRIDES-cont

Common milling techniques



Drawback: completely uncontrolled (chaotic) movement of grinding balls

CONTROLLED REACTIVE MECHANICAL ALLOYING/MILLING (CRMA/MM)



Magneto-mill Uni-Ball-Mill 5 for controlled milling - trajectories of milling balls are controlled by strong NdFeB magnets

Courtesy of A.O.C. Scientific Engineering, Australia

Mg-M-H SYSTEMS SELECTED FOR SYNTHESIS BY CRMA

Mg-2B (crystalline)(c)-H	$Mg(BH_4)_2$ or MgB_2H_8
Mg-2B (amorphous)(a)-H	
2Mg-Co-H	Mg_2CoH_5
3Mg-Mn-H	Mg_3MnH_7
2Mg-Fe-H	Mg_2FeH_6

Complex metal hydrides: mixed ionic-covalent bonding between metal and hydrogen complex, e.g. $(FeH_6)^{4-}$

EXPERIMENTAL OUTLINE-Milling

1.Elemental powders of Mg, B (cryst&amorph.), Co, Mn and Fe.

3. Handling of powders in the glove bag filled with helium for environmental protection.

4. Milling in the magneto-mill Uni-Ball-Mill 5; ball-to-powder weight ratio (BPWR) was 10:1 for the 2Mg-Co and 3Mg-Mn mixtures and ~40:1 for the other mixtures.

3.Hydrogen pressure in the milling vial 400-500 kPa

5. Working distance WD= 10 to 3 mm depending on the specific alloy; it governs the force of the magnetic attraction exerted onto the steel balls.

EXPERIMENTAL OUTLINE-
Microstructural and thermal studies

- **High-resolution field emission SEM (FE SEM) LEO 1530 with integrated EDAX Pegasus 1200**
- **X-ray diffraction (XRD) using Philips PW 1730 and Siemens D500 diffractometers; CuKα radiation (λ=0.15418 nm)**
- **Differential scanning calorimetry (DSC) (Netzsch 404); heating rate 4 K/min; argon flow rate 16ml/min**
- **Thermogravimetric analysis (TGA)(TA Instruments); heating rate 10 K/min; helium flow**

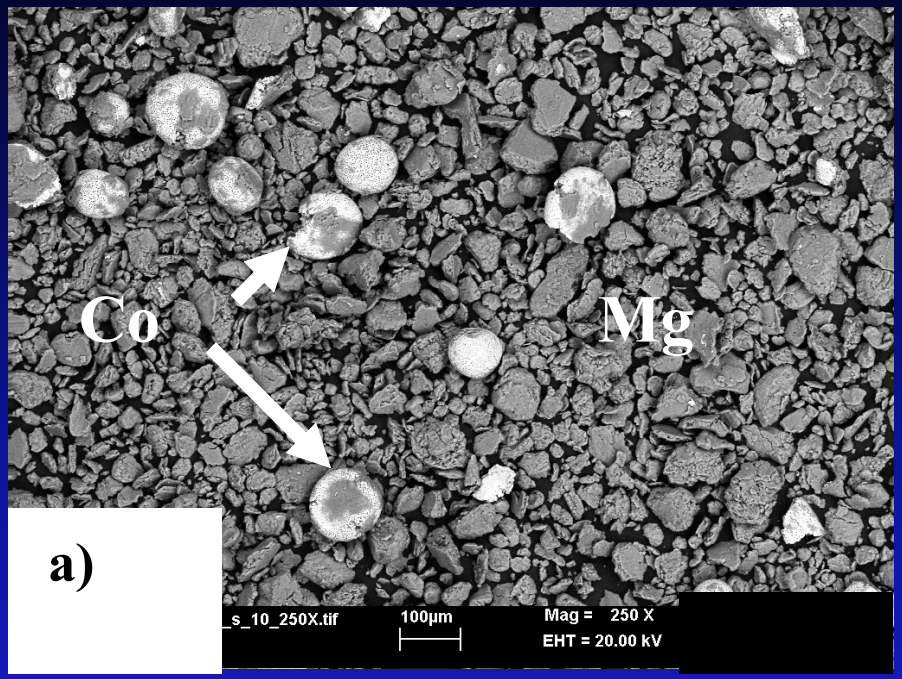
EXPERIMENTAL OUTLINE-
Nanograin size calculations

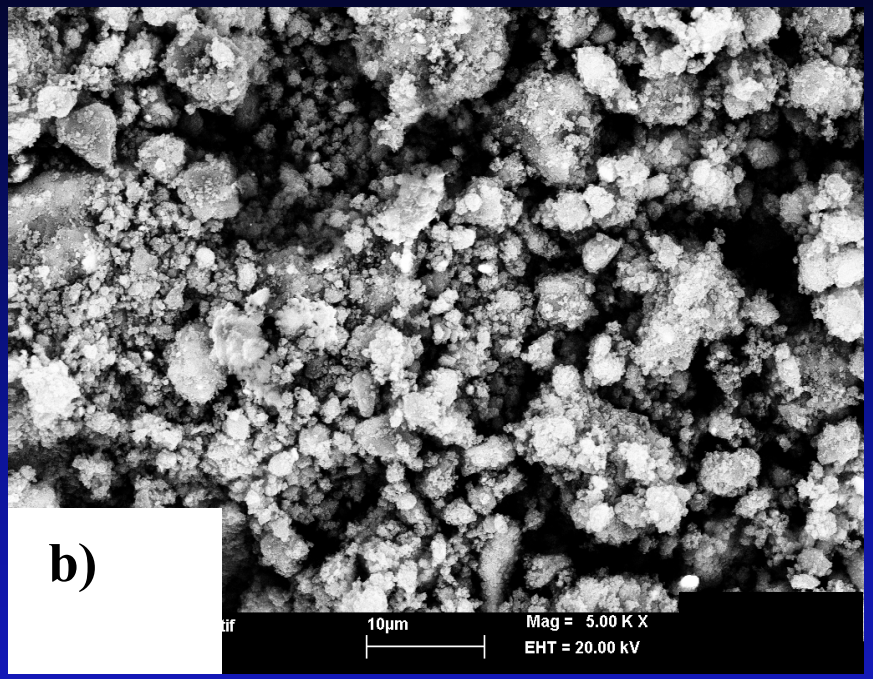
From XRD peak broadening using linear regression procedure (Klug&Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, John Wiley & Sons, New York (1974).

$$\frac{\delta^2(2\theta)}{\tan^2\theta} = \frac{K\lambda}{L}\left(\frac{\delta(2\theta)}{\tan\theta\ \sin\theta}\right) + 16e^2$$

L-nanograin (crystallite) size; e-lattice strain; λ-the wave length; θ-position of the analyzed XRD peak maximum; K-constant; $\delta(2\theta)=B(1-b^2/B^2)$(rad)-the instrumental broadening-corrected "pure" XRD peak profile breadth; B and b-FWHM (full width at half maximum) of analyzed and reference peak, respectively

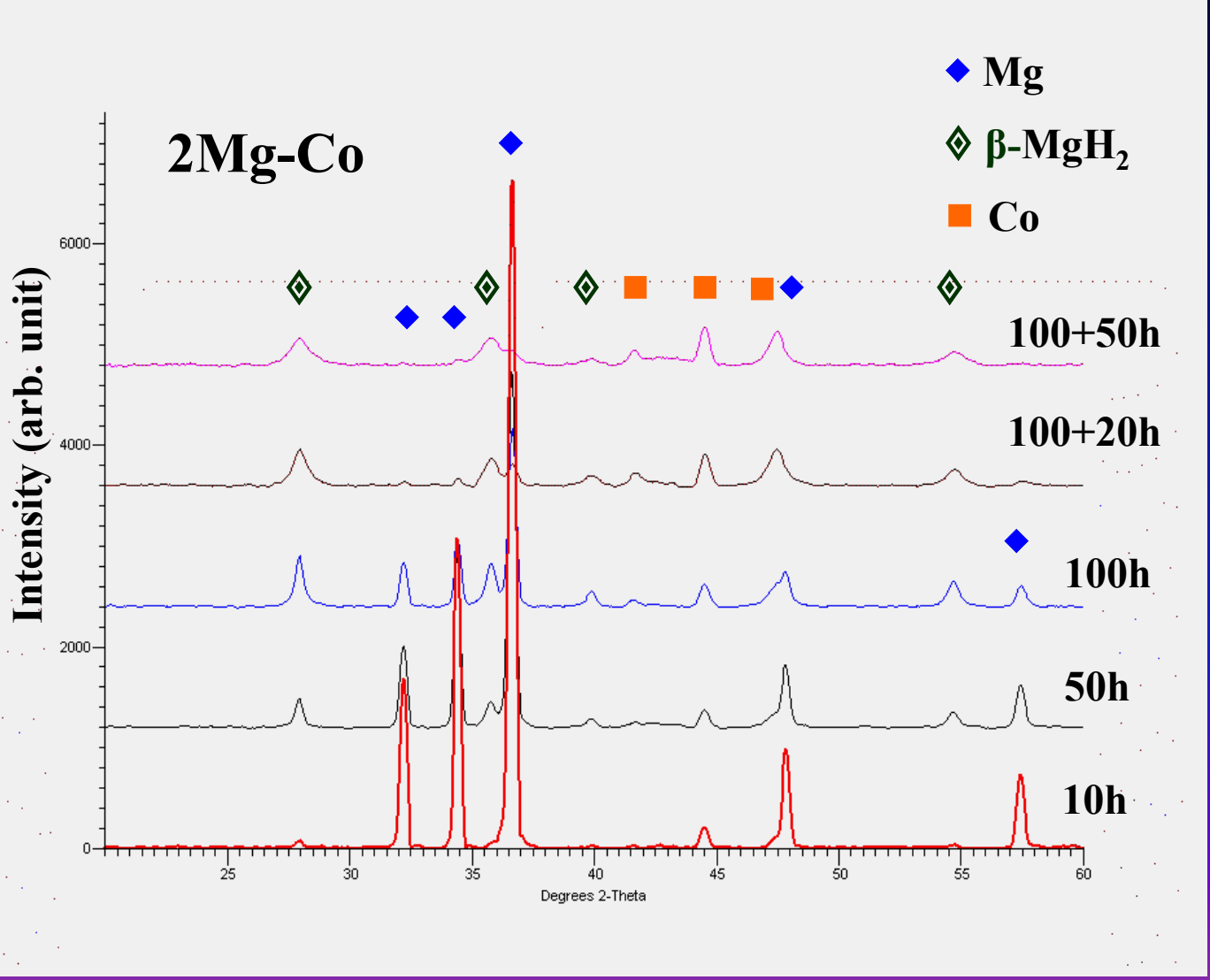
RESULTS-Microstructure of powders





Backscattered electron (BSE) images of the morphology of powders processed under shearing mode by CRMA under hydrogen. a) 2Mg-Co mixture milled for 30h using WD=10 mm and BPWR=10:1 and b) Mg-2B (crystalline *(c)* boron) mixture milled for 5h using WD=5 mm and BPWR=44:1. RPM=60 applied during milling.

RESULTS – XRD patterns vs. milling time



Typical for

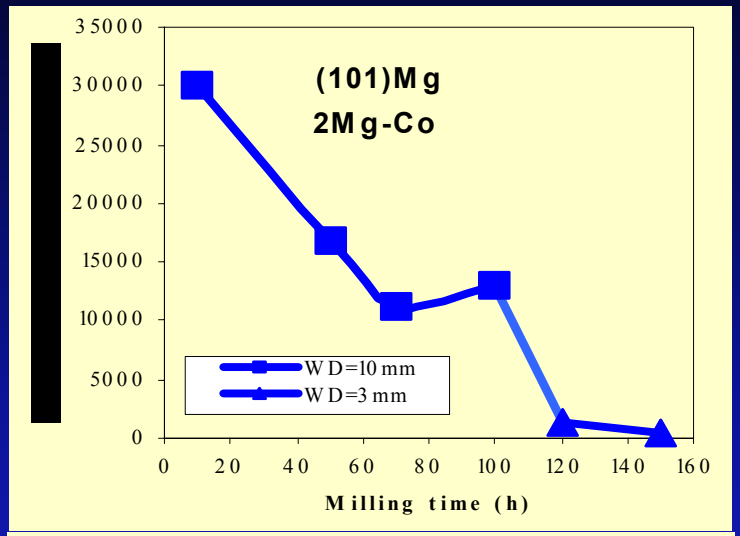
2Mg-Co

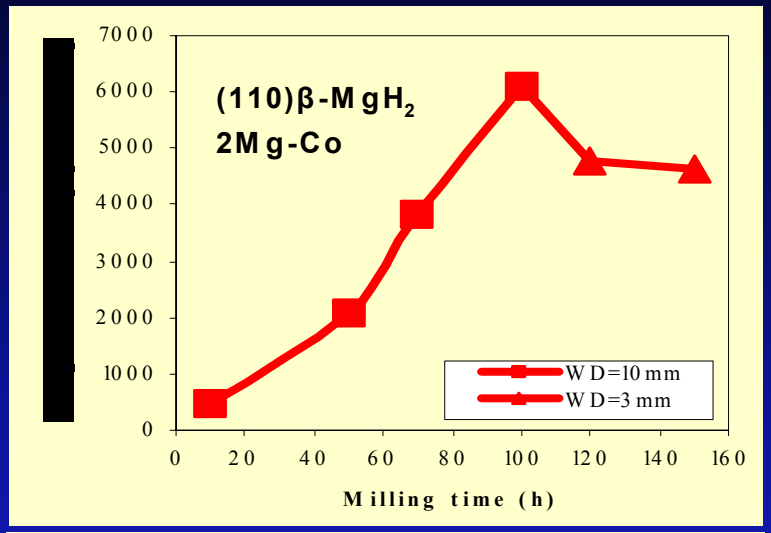
Mg-2B

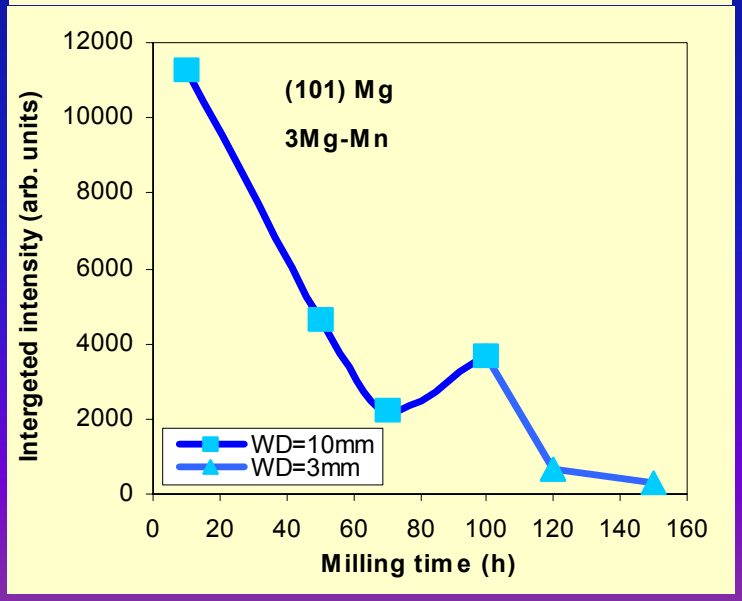
3Mg-Mn

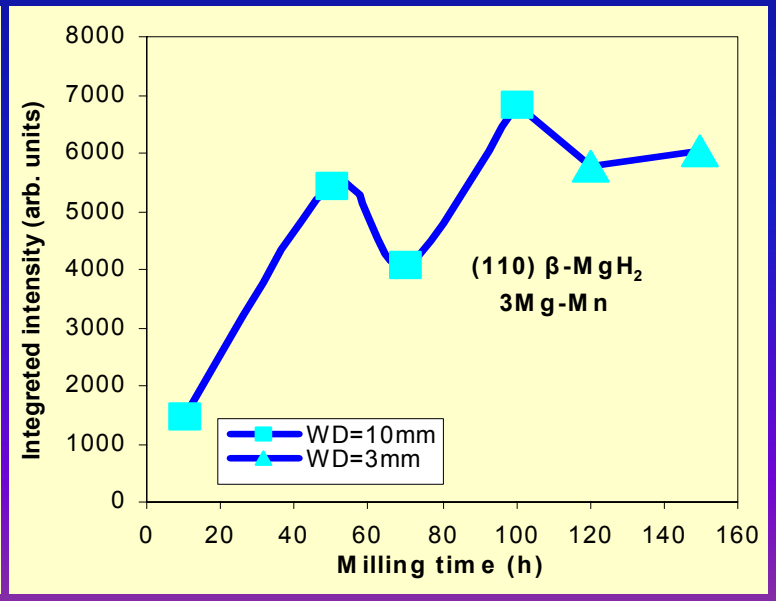
systems

RESULTS- XRD intensities vs. milling time









Mg consumed almost completely to form

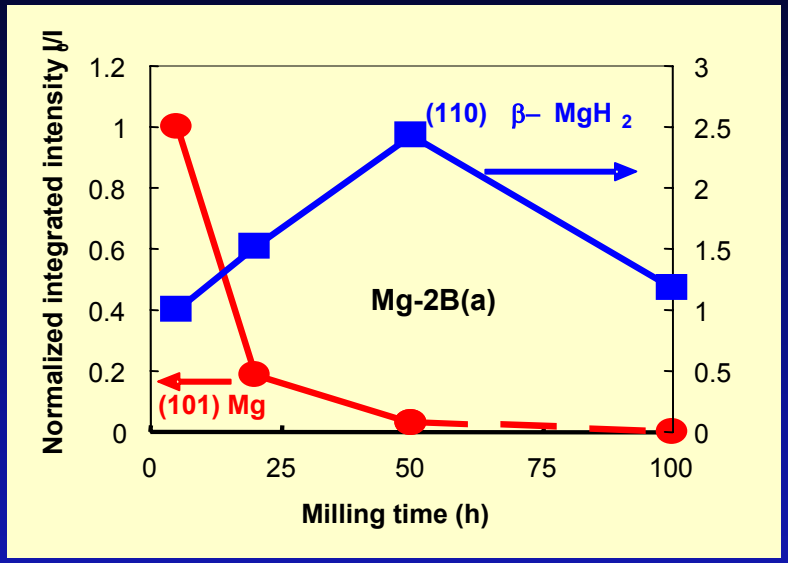
β-MgH_2

in

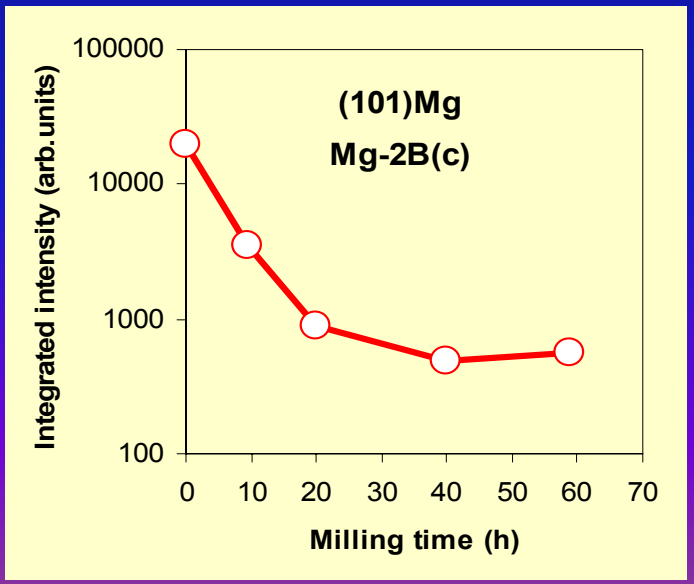
2Mg-Co

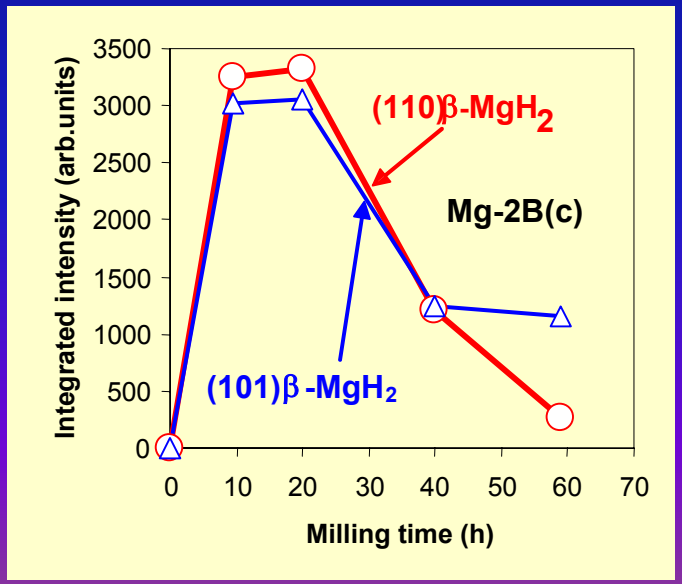
3Mg-Mn

RESULTS-XRD intensities vs. milling time (cont.)

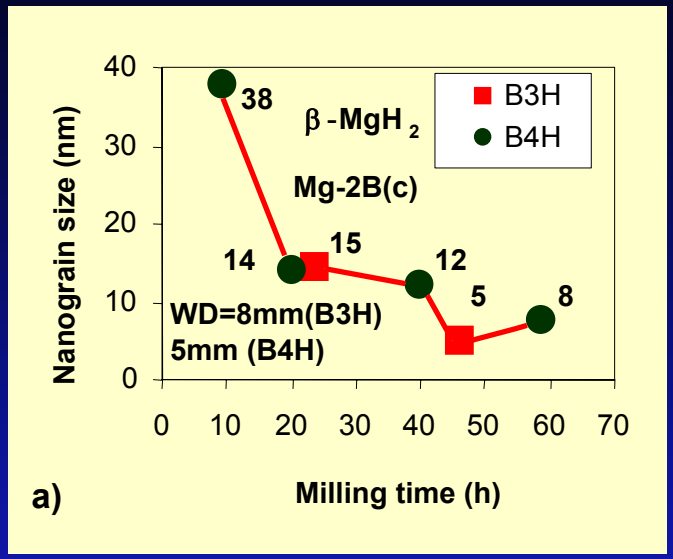


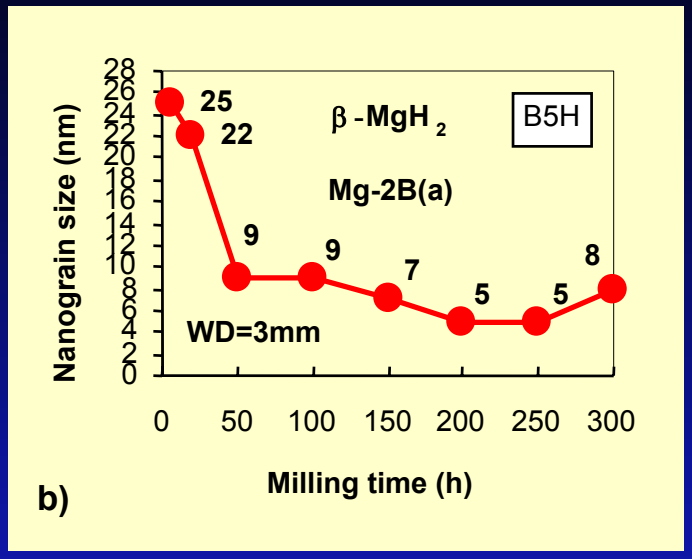
- Mg-2B(a)-complete consumption of Mg to form β-MgH_2 (at 50h)
- Mg-2B(c)-incomplete consumption of Mg to form β-MgH_2
- Partial amorphization (?) of β-MgH_2 after 50 and 20h of CRMA, respectively

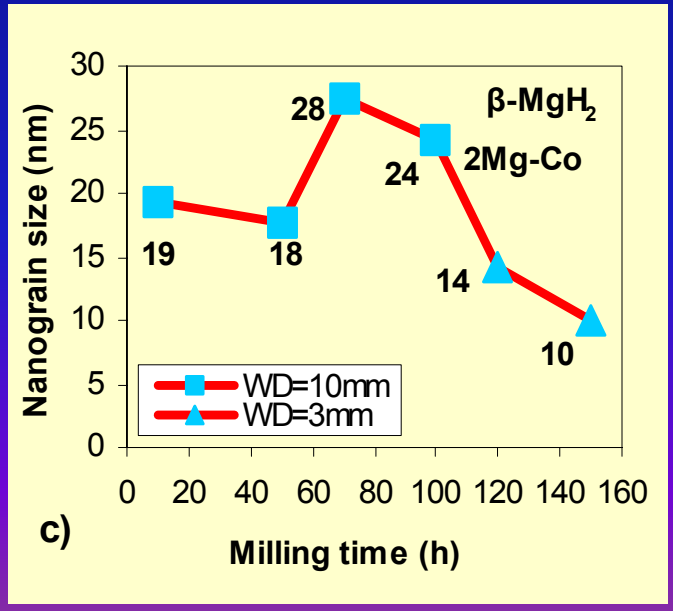


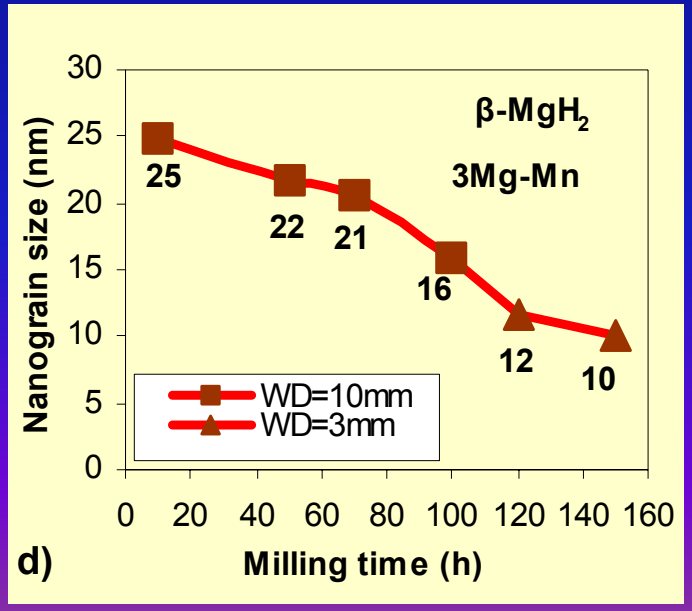


RESULTS-Nanostructured β-MgH_2 hydride



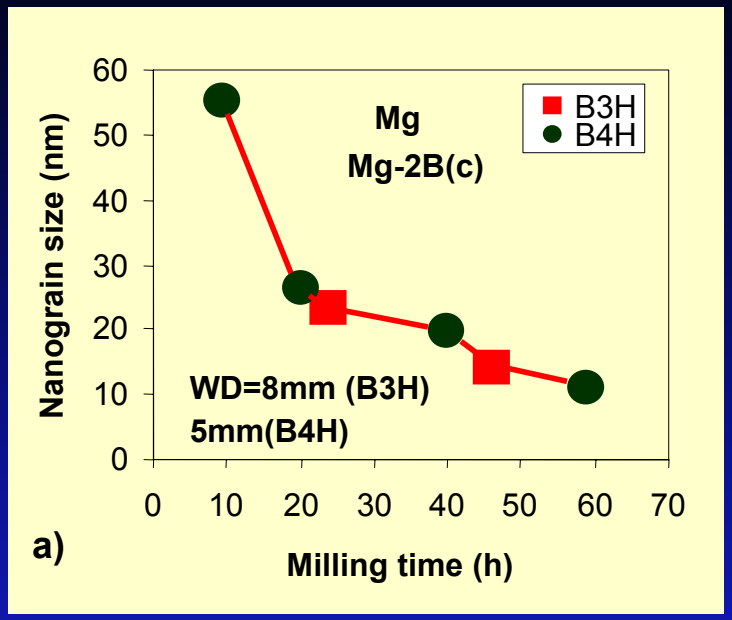


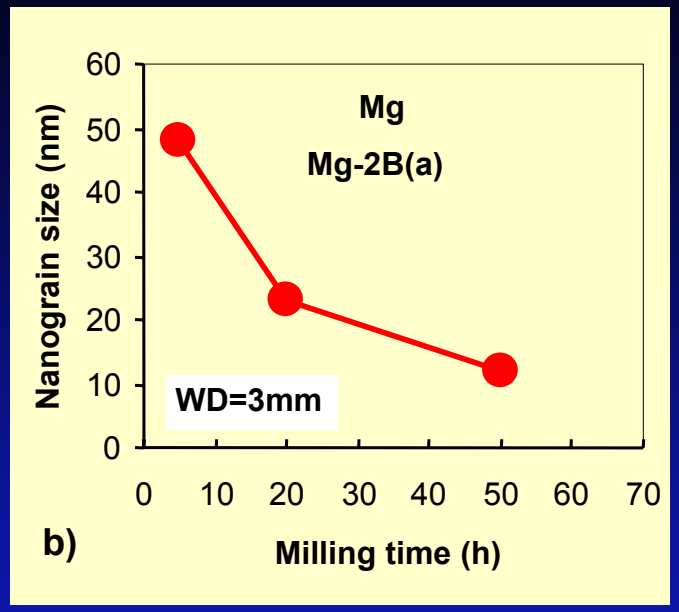




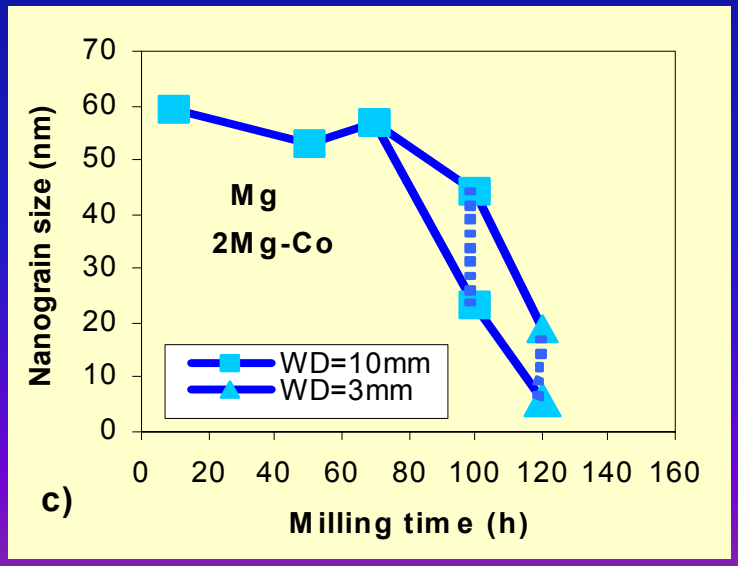
Principal hydride in 2Mg-Co, 3Mg-Mn and Mg-2B is nano-β-MgH_2

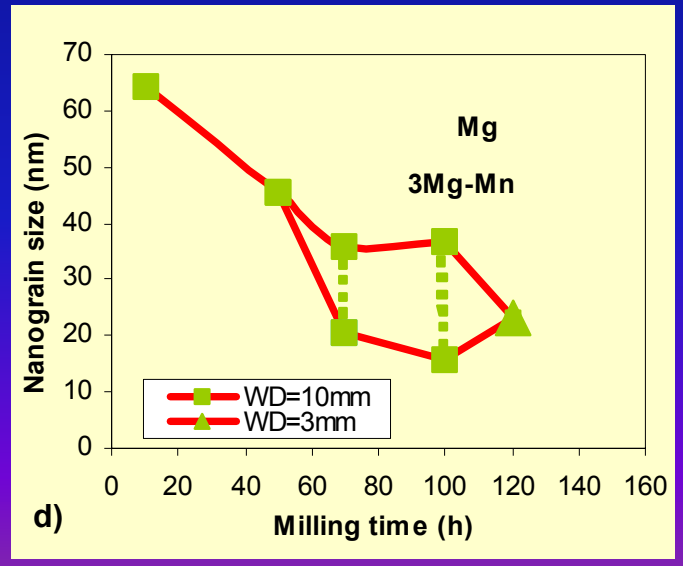
RESULTS-Nanostructured Mg





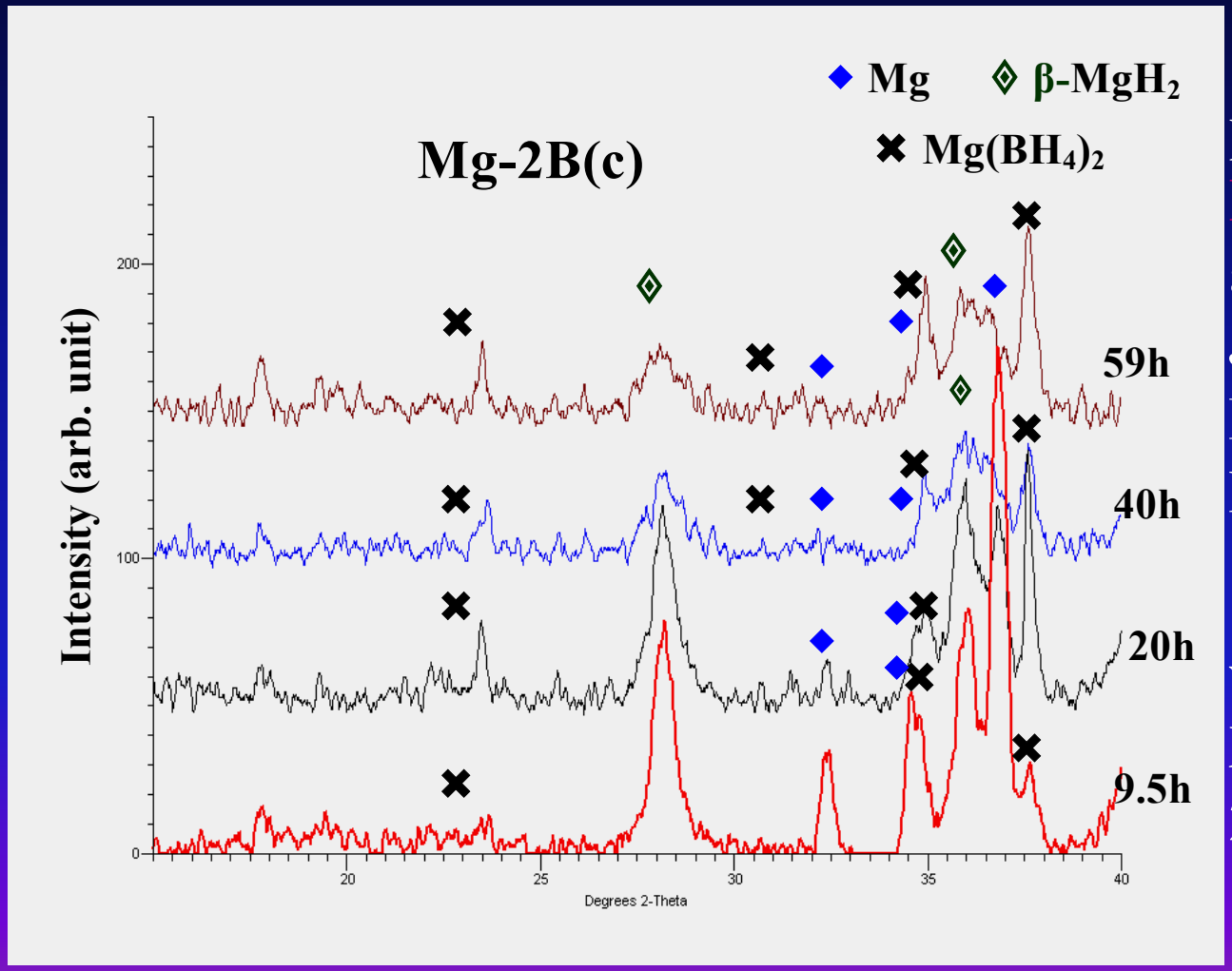
Nanocomposite $Mg+\beta\text{-}MgH_2+[Mg(BH_4)_2?]$ up to 50-60h of milling





Nanocomposite $Mg+\beta\text{-}MgH_2$ + (remnant Co; Mn) up to 120h of milling

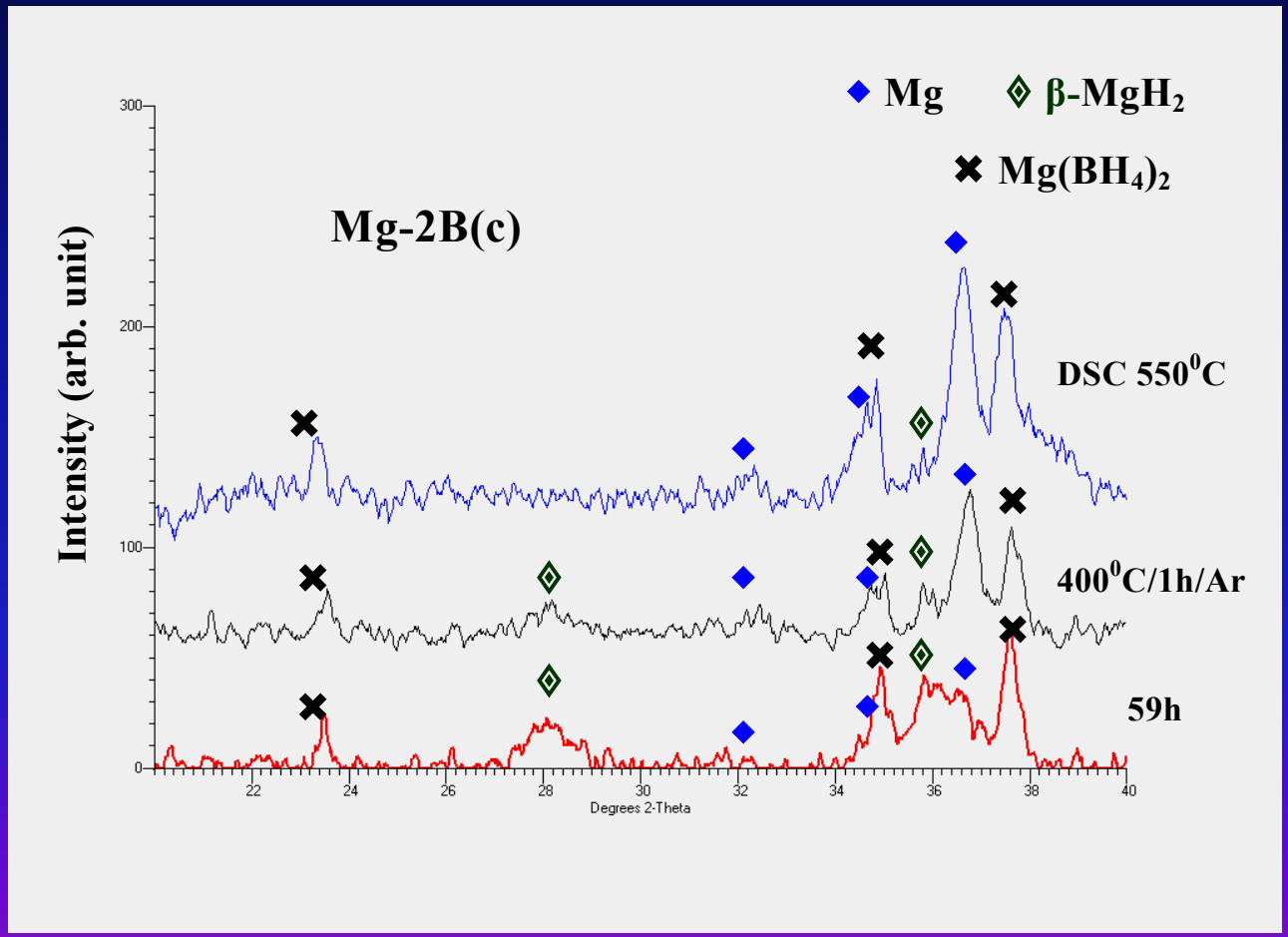
RESULTS-Nanostructured $Mg(BH_4)_2$ in Mg-2B(c) system



✖shows the exact peak position for $Mg(BH_4)_2$ according to JCPDS Powder Diffraction File No.26-1212

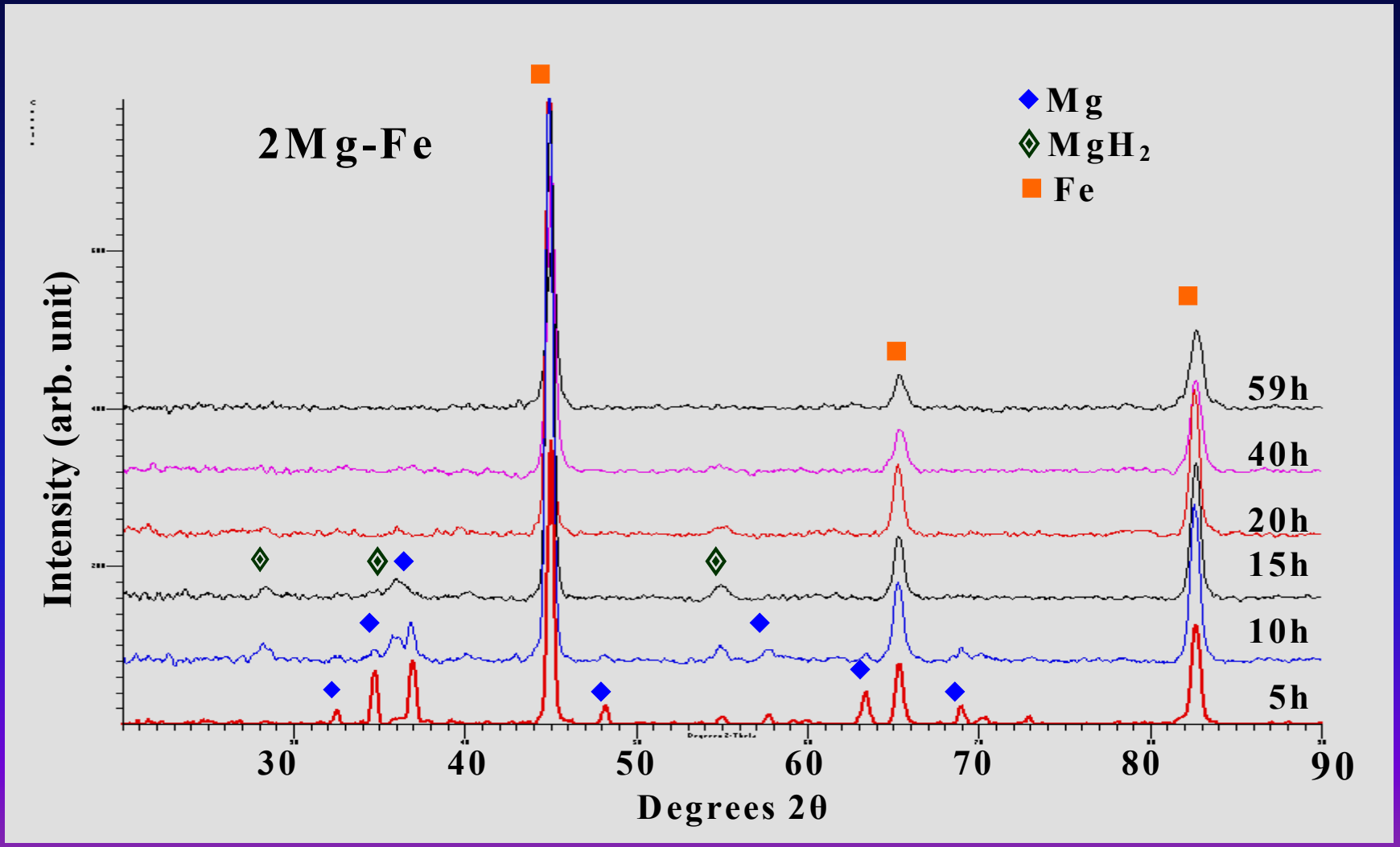
[similar peaks but weaker also in XRD from Mg-2B(a)]

RESULTS - Nanostructured $Mg(BH_4)_2$ –XRD after thermal analysis

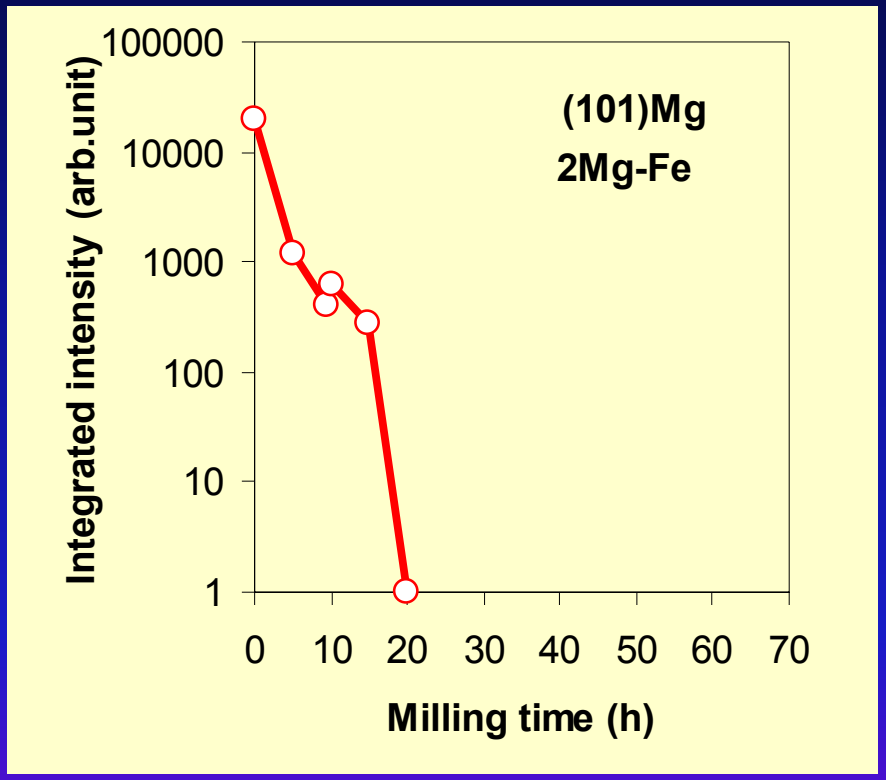


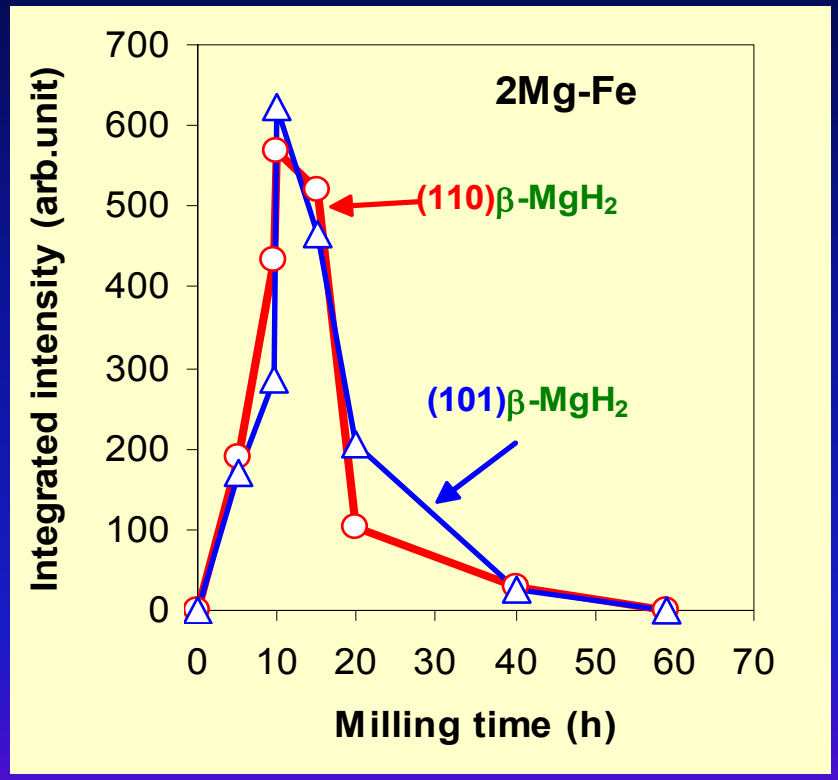
Thermally stable hydride?

RESULTS - Amorphization in the 2Mg-Fe-H system - XRD pattern



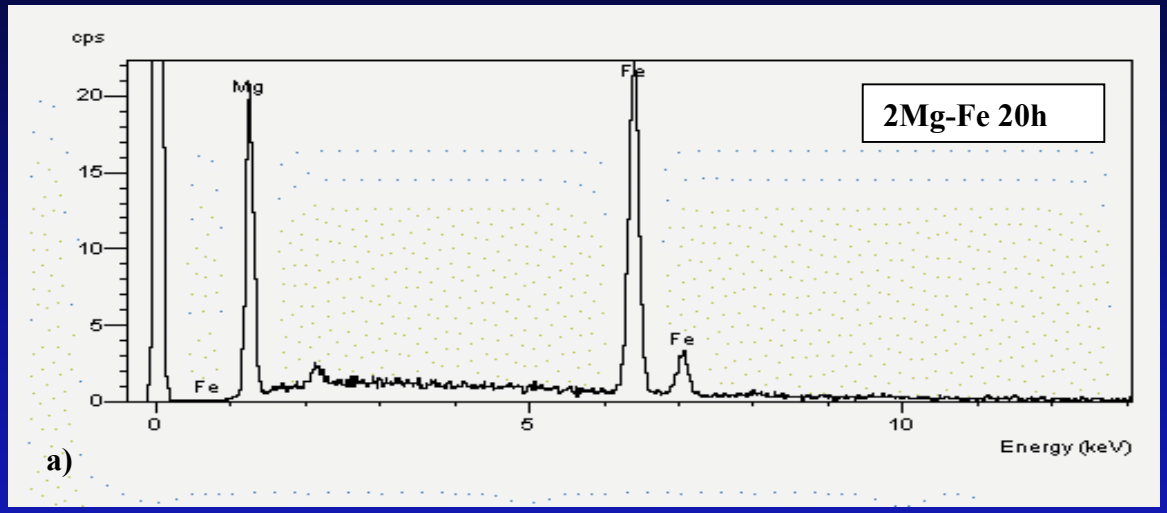
RESULTS - Amorphization in the 2Mg-Fe-H system - XRD intensities

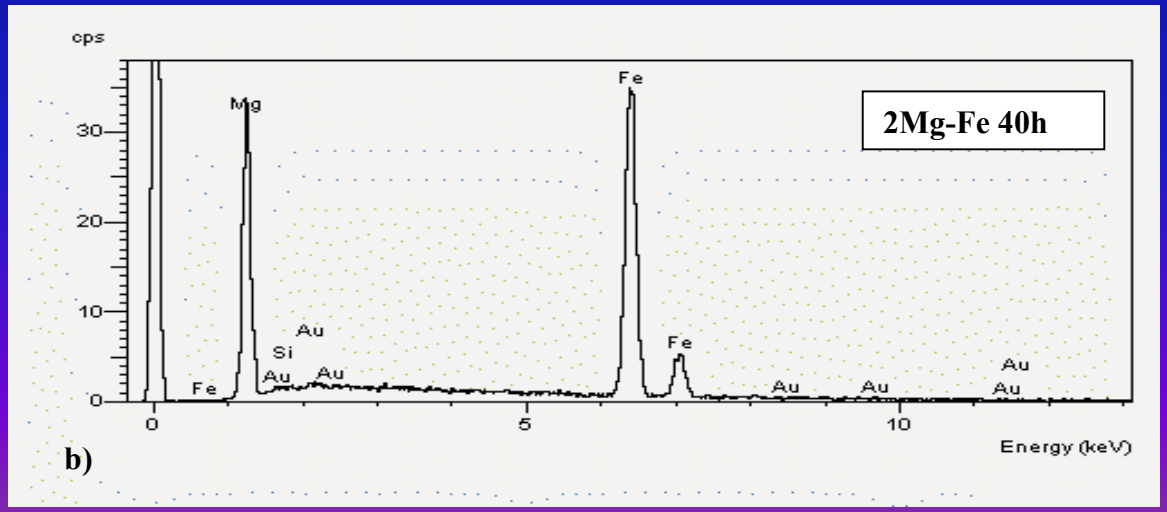




Amorphization of Mg and β-MgH_2!

RESULTS - Amorphization in the 2Mg-Fe-H system – Qualitative EDS

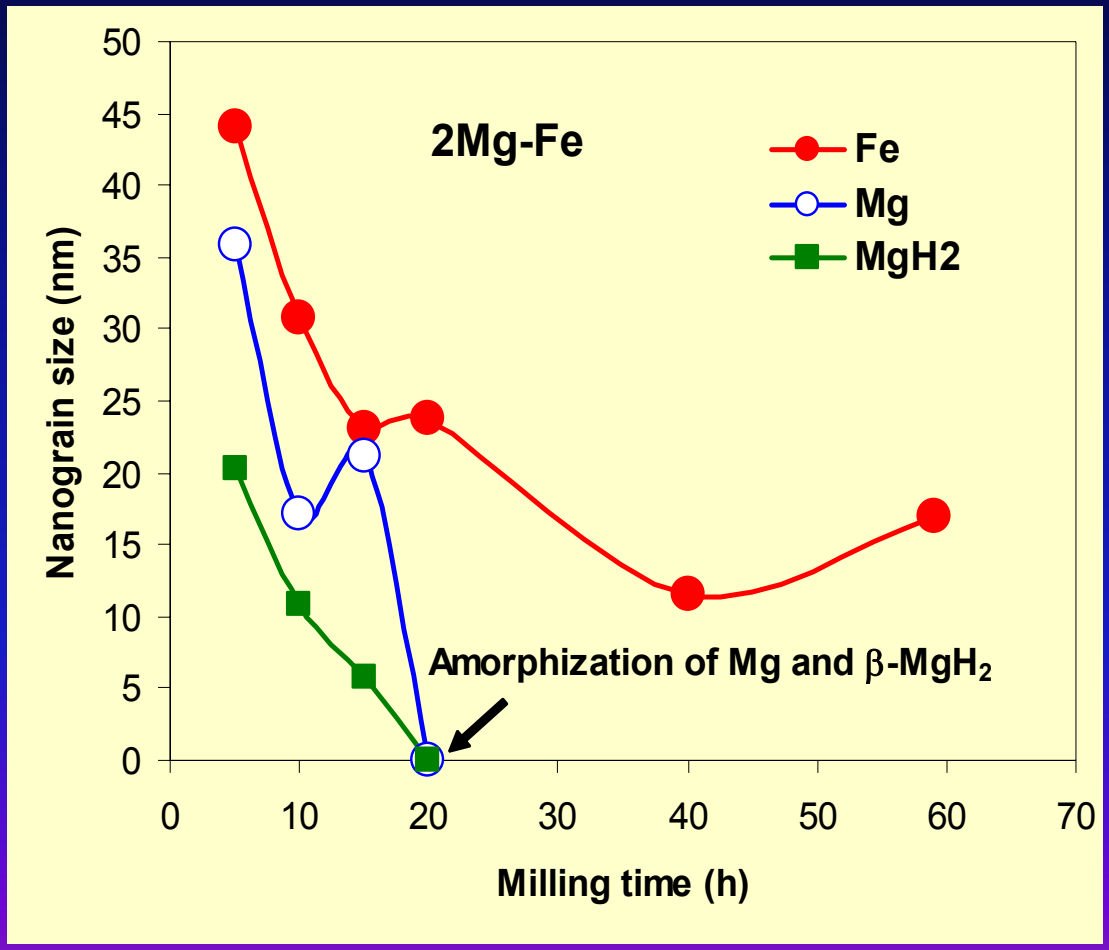




Mg peak clearly seen in EDS profile but absent in XRD:

Mg exists in the *amorphous* state

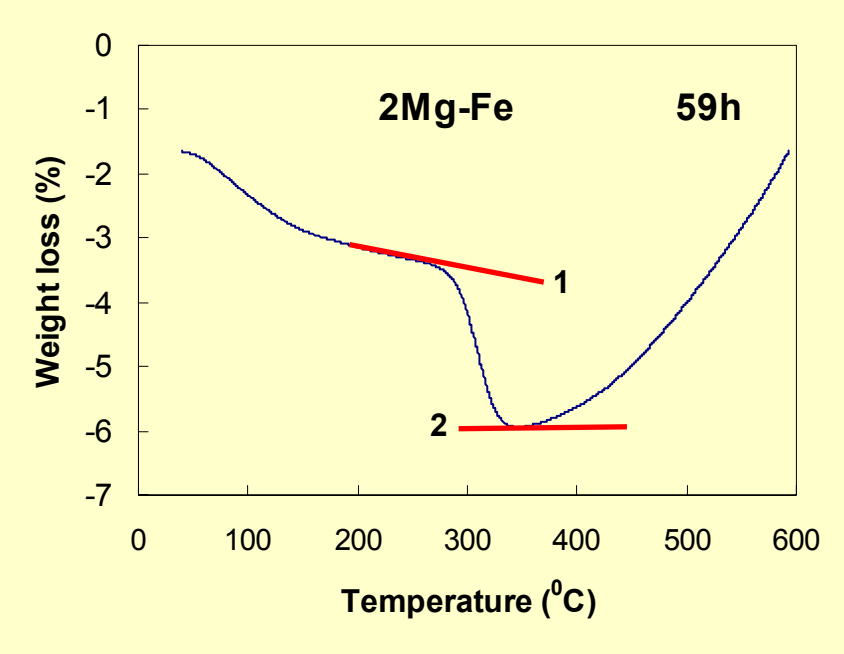
RESULTS - Amorphization in the 2Mg-Fe-H system - Nanograin size/nanocomposite

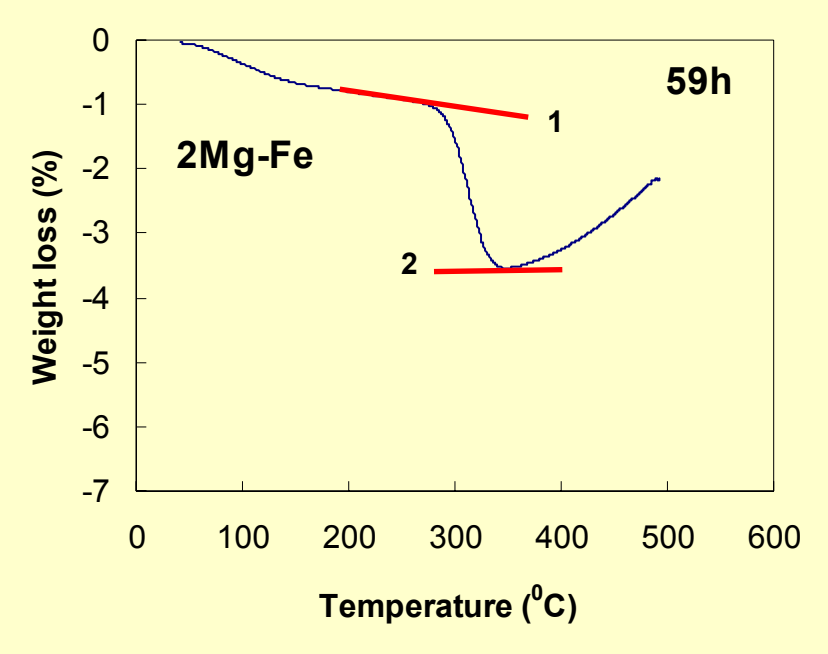


Oleszak&Shingu,Mater. Sci.Forum 235-238 (1997) 91-96

Critical average nanograin size favorable to the formation of amorphous phase is on the order of ~10 nm

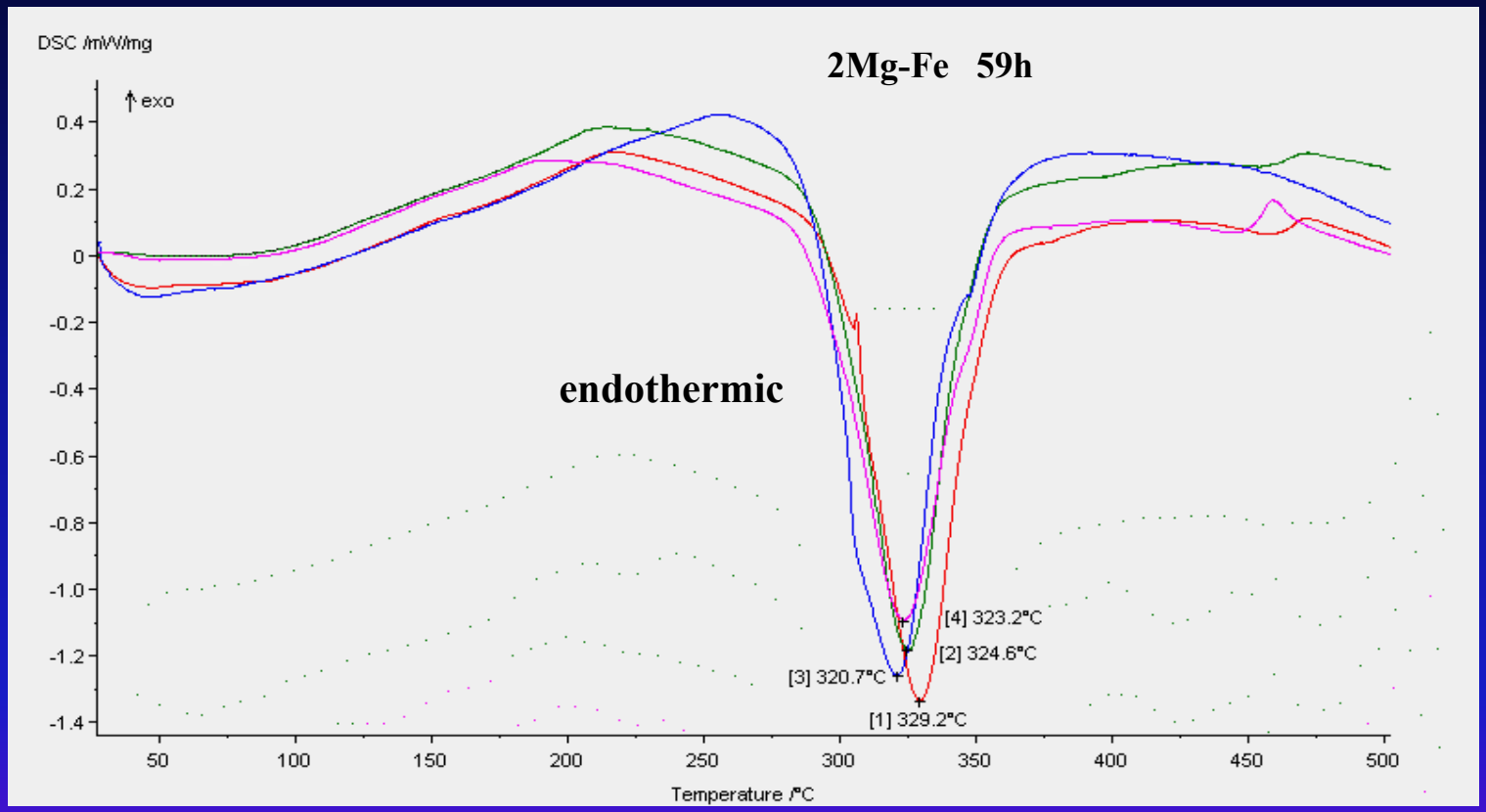
RESULTS - Amorphous hydrides in the 2Mg-Fe-H system – Thermal behavior-TGA





Desorption from amorphous hydrides: range 2.21-4.16wt% between tangent lines 1 and 2 from all TGA runs

RESULTS - Amorphous hydrides in the 2Mg-Fe-H system – Thermal behavior-DSC



Peak temperature range: 320.7 -329.2^{0}C – agrees well with TGA

RESULTS - Amorphous hydride in the 2Mg-Fe-H system – stoichiometric formula

Based on the results of desorbed hydrogen observed in TGA runs which was in the range 2.21-4.16wt% the stoichiometric formula of the amorphous hydride can be estimated as $MgH_{0.6\text{-}1.1}$. The hydrogen-to-metal ratio in this formula is nearly 1 which implies that the amorphous hydride has a *metallic* character. This is in excellent agreement with Orimo et al [Acta mater. 45 (1997) 2271-2278] who reported that amorphous hydrides in various systems have the hydrogen-to-metal ratio ~1 and metallic character.

SUMMARY/CONCLUSIONS

1. **A principal nanostructured hydride formed in 2Mg-Co, 3Mg-Mn and Mg-2B mixtures is β-MgH_2; no Mg_2CoH_5 and Mg_3MnH_7 complex hydrides have been formed during CRMA under *shearing* mode despite a profound nanostructurization of elemental species in the mixture (*Question: why no formation of complex hydrides has occurred?*)**

2. **XRD peaks close to the peaks from $Mg(BH_4)_2$ are observed on the scans from the Mg-2B(crystalline) mixture and on the scans (but weaker) from the Mg-2B(amorphous) mixture**

SUMMARY/CONCLUSIONS (cont.)

3. **In the 2Mg-Fe mixture there is initially a gradual *nanostructurization* of the Mg and β-MgH_2 phases followed by *amorphization* of both phases with increasing milling time. Eventually the amorphous hydride, possibly with the stoichiometric formula $MgH_{0.6-1.1}$, is being formed; no formation of complex hydride Mg_2FeH_6 is observed**

   (Question: why no formation of Mg_2FeH_6 has occurred (successfully synthesized by some other researchers) and instead an amorphous hydride has been formed ?

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